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Dissolved Elemental Mercury Investigations in Long Island Sound Using On-Line Au Amalgamation-Flow Injection Analysis

C.-M. TSENG,*,†,‡ P. H. BALCOM,‡ C. H. LAMBORG,‡ AND W. F. FITZGERALD‡

National Center for Ocean Research, National Taiwan University, P.O. Box 23-13, Taipei, Taiwan, 106, Republic of China, and Department of Marine Sciences, University of Connecticut, Groton, Connecticut 06340

A novel semiautomatic dissolved elemental mercury analyzer (DEMA) was developed for investigating dissolved elemental Hg (DEM) in natural waters. This on-line setup couples the main analytical steps from sample introduction, gas−liquid separation, and Au amalgamation/separation to final detection/data acquisition using flow injection techniques. This approach provides ease of operation and high analytical performance and is suitable for shipboard use. The analyzer can be fully automated and also be modified to examine other Hg species (e.g., reactive and total Hg and monomethyl-Hg). Here, we present the results of laboratory performance tests and make a comparison with a traditional manual method. DEM measured by both manual and the DEMA show good agreement. Representative field DEM data from spring and summer 1999 in Long Island Sound, U.S.A. (LIS) are presented. Spatial and temporal DEM variations were evident. Rapid and accurate determinations of DEM are necessary to observe its distribution dynamics, evaluate emissions, and assess its role in the aquatic biogeochemical cycling of Hg.

Introduction

Dissolved elemental mercury (DEM) is an important mercury (Hg) species in natural waters. Its aquatic biogeochemistry includes in-situ formation resulting in supersaturation with respect to the atmosphere, which in turn can lead to significant emission at the water−air interface. These processes decrease the amount of Hg available in aquatic ecosystems for methylation and subsequent bioaccumulation. For example, Rolfhus and Fitzgerald (*1*) recently demonstrated that DEM production (e.g., 0.4% to 3.5% d^{-1} of dissolved total Hg) and evasion (80 ± 25 kg yr^{-1}, 35% of total annual Hg inputs) exert a major control on the behavior and fate of Hg in Long Island Sound, New York−Connecticut (LIS, NY−CT), and by implication other coastal regions. DEM levels depend on production and evasion rates, which are regulated by environmental factors (e.g., Hg substrate, reducing agents, and climatological conditions). Hence, distributional patterns within a productive near shore system such as LIS should exhibit temporal (e.g., seasonal) and spatial variations. Rapid and reliable measurements of volatile DEM are therefore critical to an improved understanding of Hg biogeochemistry, especially in biologically productive and understudied coastal marine environments. Traditional approaches to DEM determination require potentially excessive handling and storage and can be tedious. To obtain an accurate evaluation of Hg emissions and observe its distributional dynamics, we have developed a new technique for fast and reliable measurement of DEM.

The determination of DEM is difficult and analytically challenging. First, the concentration of DEM is extremely low, ca. fM, so that ultraclean sampling and proper analytical techniques (e.g., purging, preconcentration, separation, desorption, and quantification) are required (*2*−*6*). Second, problems such as contamination and DEM loss/oxidation could occur during sampling and storage (*7*). Third, the DEM distribution may be highly dynamic so that real-time, shipboard measurements are needed. Commonly used methods based on the "two-stage amalgamation" approach (*2*), for instance, involve manual handling of preconcentrated samples as well as analytical setups that are not hyphenated (analytical apparatus directly connected together), resulting in an analysis time over 30 min per sample (*4*−*6*, *8*, *9*) and an increased risk of leaks in the analytical train during purging and analysis. Additional concerns include blank control, potential contamination by laboratory air containing high Hg levels, and DEM losses during sample introduction. In general, the traditional manual approaches do not fulfill the analytical and field requirements in an efficient manner (i.e., there are major drawbacks related to quality control, duration of analysis, complexity, and reliability).

Our DEM analyzer (DEMA) is a simple, robust, on-line purge and trap system combining flow-injection and dual gold amalgamation preconcentration techniques together with cold vapor atomic fluorescence detection and is well-suited for shipboard use or in other field and laboratory situations. It has been used in studies of DEM in LIS since 1999. Analytical operation is simple, and manual handling of samples is minimized. With additional valves, multiple sparging systems may be operated simultaneously giving high sample throughput. Good recoveries (n = 20, >95%) and replication (N = 10, rsd <5%) are achieved. There is no risk of contamination with ambient air because the analyses are conducted within a closed circuit. Common interferences from organic-rich samples and water vapor are readily eliminated. Below, we describe the DEMA and its reliability/performance in laboratory and field tests. In addition, selected spring and summer DEM results from LIS are presented, and these include distributional patterns and evasional fluxes.

Experimental Section

Sampling Site and Procedures. Long Island Sound is one of the "Great Waters" of the United States and one of the world's most important commercial and recreational coastal resources. It is a large embayment (surface area, 3200 km^2; water volume, 6.2 × 10^{10} m^3), bordering the states of Connecticut and New York (Figure 1). The significant annual freshwater supply to LIS is mainly from the Connecticut River (eastern zone, about 70% of the total). The East River (western LIS) transports a relatively small amount of water to LIS through tidal exchange, but it is affected by large amounts of effluent from wastewater treatment facilities (i.e., sewage). Its anthropogenic contribution may have significant regional

* Corresponding author phone: 886-2-23636364 ext 143; fax: 886-2-23644049; e-mail: cmtseng@ncor.ntu.edu.tw.
† National Taiwan University.
‡ University of Connecticut.

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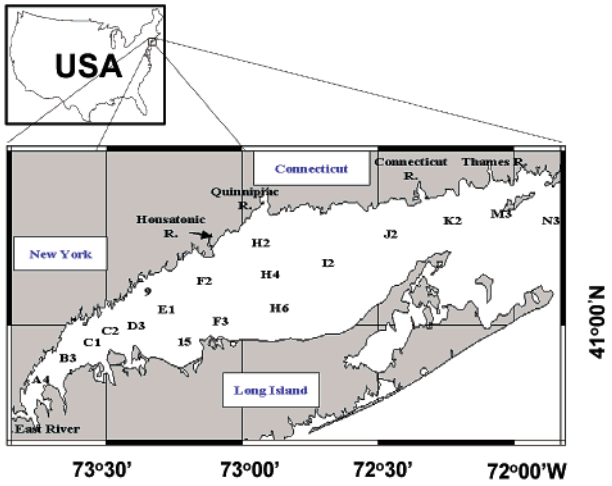

FIGURE 1. Long Island Sound with the surface sampling locations for DEM (CT DEP Water Quality Monitoring stations).

influence on the Hg content and speciation of western LIS (*10*).

The DEM investigations presented here were performed during May 5−6 and August 30−September 1, 1999, in LIS. Surface waters (ca. a depth of 1 m) were sampled from R/V *John Dempsey* by dipping 2.2-L Teflon bottles off the front of the ship using a PVC pipe (2.5-m length, 1-in. diameter). During sampling, a Teflon sample bottle was inserted in a bottle holder on the sampler; the bottle was rinsed three times with sample water and then completely filled. The bottles were capped, double-bagged, and stored in coolers under ice on deck. DEM concentrations measured using this manual sampling method agree well with those from Teflon-lined Go-Flo bottle collections (*1*, *9*). The analysis of DEM was carried out within 4−6 h after same-day transport to the laboratory. No significant storage oxidation/production of DEM was observed in our samples when held cold and in the dark (*1*, *9*). Ultraclean sampling techniques were used throughout the sample collection and analysis processes (*3*−*6*, *8*−*11*).

Reference Methodology. Details on manual procedures for DEM analysis can be found in refs *2*, *4*−*6*, and *9*. In general, two subsystems are used for DEM analysis: 1) the purging device for stripping DEM onto a gold (Au) trap and 2) an analytical setup for measuring DEM. Briefly, the analytical steps are as follows. First, DEM is collected on an Au-coated sand trap (termed the "sample trap") by purging the water samples with nitrogen (N_2) in a gas/liquid separator (GLS, "bubbler"). Second, the sample trap is removed from the purging vessel and placed into an argon (Ar) carrier stream to help remove water vapor after completion of the purging step. Third, the sample trap is then connected in series with an "analytical trap". Fourth, the elemental Hg (Hg^0) is thermally desorbed from the "sample" trap and carried onto the "analytical" trap via the Ar stream. Finally, detection of Hg^0 is achieved with a cold vapor atomic fluorescence detector following thermal desorption from the "analytical" trap, again using an Ar carrier. Such a dual amalgamation technique (*2*) has worldwide recognition and is the basis for the US EPA Standard Method #1631.

DEMA Description. The DEMA design is similar to the flow systems for alkyl-metal(loid) species analyses presented by Tseng et al. (*12*, *13*) and is depicted in (Figure 2). It combines four main procedural steps from sample introduction through detection. The device consists of two plexiglass stands (0.64 cm thickness; ca. L × W × H: 38 × 38 × 55 cm). Each includes an upright board, flat base, and triangular bracing pieces all connected with removable machine screws that allow the boards to be dismantled for transport. One board is used to hold the 2-L sample bottle and GLS, while the other board provides the mounting support for the Au traps, heating coils and valving. Heavy system components, such as transformers and timer/controller, are placed on the base of the analytical board.

Teflon tubing (mostly 3.2 mm o.d.) and fittings were used throughout. The lengths of transfer lines were minimized to prevent condensation. The general procedures of the analysis are summarized as follows.

Purge and Au Sand Trapping. One or two L of the sample, contained in a 2.2-L Teflon bottle, are transferred (PFA tubing, 6.4 mm o.d.) into the GLS (custom-made of borosilicate glass) by opening the 3-way stopcock at the base of the GLS and positioning valve 1 (V1 in Figure 2, manual 6-way injection valve, Rheodyne 5020) such that the sample bottle is pressurized with N_2 (2 bar; purified by passing it through a Au sand trap + Carbotrap) through a customized bottle cap with gastight fittings. When pressurized, the sample flows through tubing inserted into the liquid that also passes through the customized cap via a Teflon fitting drilled out to allow passage of the tubing through the fitting body. Valve 2 (V2) is also positioned so that the headspace of the GLS loads onto the first or sample trap while the sample is filling. In this way there is no chance of loss of DEM from the sample during filling and overfilling. When filled, the GLS stopcock is closed.

Purging of the sample is begun by manually turning V1 to direct N_2 through a frit (~20 μm porosity) in the bottom of the GLS, and then the purge gas loads onto the sample trap. Purge gas flow rate is nominally 1 L min^{-1}. During operation, the GLS was wrapped in aluminum foil to prevent sunlight-induced production of DEM during the purging. Samples are purged for the length of time needed to pass 15 times the volume of the sample in purge gas through the fluid (i.e., at 1 L min^{-1} for a 2 L sample, 30 min; see purging efficiency experiments below). Before being collected on the sample trap, the purge gas flows through a Teflon syringe filter (0.5 μm, 47 mm PTFE, Cole-Parmer), a precleaning trap (Quartz tubing, 3.2 mm i.d., 6.4 mm o.d., 10 cm length) packed with reagent grade soda lime (ca. 0.4 g, 14−24 mesh, Fisher ChemAlert), and then Tenax-TA (ca. 0.03 g, 23% graphitized carbon, 20/35 mesh, Alltech) in separate sections. The pretrap is used to remove water vapor and volatile organic compounds that can degrade the collection efficiency of the Au-sand traps. The Hg in the purge gas is finally amalgamated on the packed Au-coated sand (ca. 0.25 g, 60−80 mesh) in the sample trap (quartz tubing, 13 cm length, 3.2 mm i.d.) and the purge gas vented from the system via V2. During the sample purging, V3 is positioned so that the second or analytical Au-sand trap is isolated from Ar flow, helping to minimize the blank background.

After complete purging, the purging N_2 is bypassed through a sidearm to drain the waste in the GLS out (PFA tubing, 6.4 mm o.d.) once the GLS stopcock is turned on. In addition, this step allows for drying of the pretrap (soda lime/Tenax-TA) during sample analysis while the sample trap is under Ar flow. N_2 continues to vent through the GLS and pretraps.

Thermal Desorption−Amalgamation and Detection by AFS. After completion of sample purging from the GLS, V2 is manually turned from the "trap" position (amalgamating DEM in the sample trap) to the "desorption" position (ready to desorb Hg onto the analytical trap), and V3 is turned from the isolating "stand-by" position to the "trap/desorb" position. After 1 min of flow stabilization, Hg trapped on the sample trap is desorbed by heating to ~600 °C by powering a Nichrome heating coil wrapped around the trap for 2 min. The Ar stream (30 mL min^{-1}) then carries the Hg to the analytical trap. Subsequently, upon heating of this trap to 600 °C for 1 min, the desorbed Hg enters the AFS detector

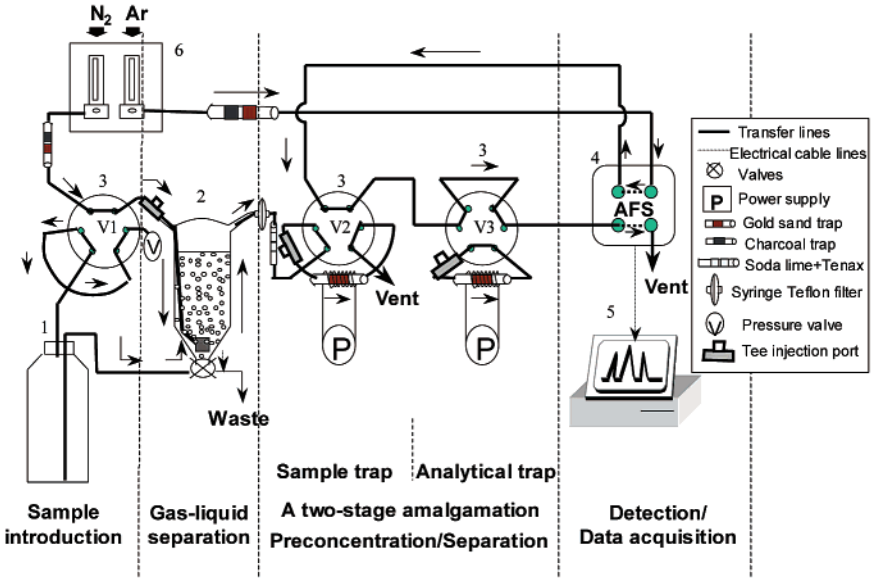

FIGURE 2. Schematic of DEMA for DEM analysis in natural waters. 1. Sampling bottle; 2. gas−liquid separator (GLS); 3. six-way injection valves (injection-V1, -V2, -V3 from left to right); 4. atomic fluorescence spectrometer (AFS); 5. integrator or personal computer; 6. flow meters.

(Tekran). Detection of Hg takes place through observation of cold vapor atomic fluorescence at 253.7 nm. The analytical signal is recorded as peak area using an integrator (Hewlett-Packard 3396A) or a personal computer with integration software (LabVIEW programmed). A fan (not shown in Figure 2) is used to cool the sample and analytical traps for 1 min following the analytical trap desorption. The whole analytical process, from flow stabilization, desorption, and detection to data acquisition, takes 5 min and is fully controlled by a programmable timer/controller (ChronTrol) that activates grounded receptacles powering heating coils and fan.

Blank and Calibration. Blanks are critical to the reliable determination of Hg at ultratrace levels in natural waters. Low blanks for DEM analysis require conditioning the Au traps, precleaning traps, and the GLS. In our routine procedures, newly packed Au columns are heated to ~600 °C for 30 min in a Ar carrier flow of 30 mL min^{-1} to remove Hg from the column. The soda lime and Tenax precleaning trap is blanked by heating at 150 °C with N_2 flow of 30 mL min^{-1} for 30 min after placing the trap in-line with a GLS and sparging a 1% HNO_3 solution for 24 h. When beginning each analysis session, we blank Au traps initially by heating at 600 °C and then blank the bubbler by purging. The trap blank is generally higher in the initial analyses, due to in-situ production of Hg^0 on the Au sand trap since the last analysis session (Tseng et al., unpublished data). The purging blanks are higher also in the first few purging tests and then decrease to an acceptable level (≤100 fmol). Once the purging blank is low and stable, analysis of real samples may begin. The procedural blank is determined by a second purging and analysis of a sample. Generally, procedural blanks were determined once every three samples analyzed. The GLS and sample introduction tubing are cleansed at the end of each analytical day using dilute HCl and HNO_3 and are thoroughly rinsed with DI water prior to subsequent use.

Calibration was performed before and during sample analysis by injecting a known mass of Hg^0 vapor (aliquot of headspace over a droplet of pure liquid Hg, sampled with a Hamilton gastight syringe (*14*)). The Hg was injected into either the Ar carrier or N_2 purging stream through a Teflon injection tee (containing a Teflon-faced silicone septum) just upstream of the sample or analytical traps or into the N_2 purging stream just before the GLS. When the injections were made upstream of the Au sand traps, excellent calibration ($r^2 > 0.995$) and high precision (rsd < 5%, $N = 10$) were obtained. When injections were made upstream of the GLS, the recoveries were generally higher than 95%. If trap recoveries fell below 85%, the old columns were repacked and reconditioned as described above. Sample trap recovery tests were conducted with injections in either the carrier stream or in purging stream once per three samples.

Preparation of DEM Synthetic Standard Solution. Optimization experiments with the DEMA were performed by analyzing Milli-Q water and coastal estuarine water (LIS water, Salinity 15−30 ppt, DOC 100−300 μM) spiked with different known amounts of Hg^0 (ca. 2.5, 5, 10, and 25 pmol). These experiments were performed within 2 days of the spiked solution preparation. A reference blank solution of Milli-Q water prepurged for 30 min at 1 L min^{-1} with purified Hg-free N_2 (activated charcoal and Au-sand trap) was also analyzed.

The spiked standard solutions were prepared in the following way: a known amount of Hg^0 vapor, obtained as for calibration, was injected into a 23-L sealed polyethylene carboy (Nalgene), filled with either Milli-Q or LIS water, through a gastight cap fitted with an injection port similar to the injection tees described above. The solution was agitated vigorously 3 times for 5 min periods to ensure complete homogeneity. The solution was then refrigerated for 1 h and shaken 3−4 more times before use. Given the large solution to headspace volume ratio, the mass loss of Hg to volatilization within the carboy was minimal.

Results and Discussion

Optimization of the DEMA. Optimization experiments were conducted in the following areas: trap and purging efficiencies and evaluation of analytical performance (blank, recoveries, precision, and accuracy).

Trap Efficiencies. The system trap components (e.g., Au, Au-coated sand, Carbotrap, Tenax, and Teflon syringe filter) were examined for their Hg adsorping properties in an Ar carrier gas stream of a dual amalgamation gas train at a constant flow of 200 mL min^{-1} with a spike of ca. 5 pmol Hg^0. The data show that only traps packed with Au material (Au or Au-coated sand) have complete trapping efficiencies (*2*). Sample stream conditioning components such as Carbotrap and Tenax (~0.15 g, used to trap organic molecules) and Teflon filters (used to remove water vapor) do not adsorb significant amounts of Hg^0 (<1%, $N = 3$).

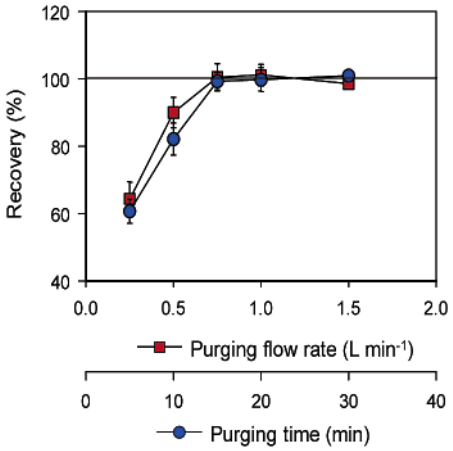

FIGURE 3. Effects of purging times (circle) and N_2 flow rates (square) on the purging efficiency for DEM. Purging time tests were done with 1 L of aqueous solution at 1 L min^{-1}. Purging flow rate tests were done with 1 L of solution at a constant purging time of 20 min.

Trapping efficiency in the full DEMA assembly (Figure 2, including a Teflon syringe filter and a precleaning trap) was also conducted. For this experiment, 1 L of spiked LIS water (salinity 23; ~0.6 pM of DEM concentration) was analyzed. The results show that high trap efficiency (>95% during 20 consecutive measurements) was obtained by Au-coated sand (~0.25 g) with the following operational conditions: purging time of 20 min and N_2 flow rate of 1 L min^{-1}. These tests confirmed that Au-coated sand traps Hg well in this application and that the Teflon syringe filter and precleaning trap do not significantly interfere with accurate determination of DEM.

Purging Efficiencies. Two factors were examined for their control on purging efficiency: 1) the purging time and 2) the flow rate of the purge gas used. Purging efficiency for DEM was tested by analysis of spiked Milli-Q water, containing ~1.3 pM of DEM. The results, presented in Figure 3, show that complete stripping of DEM takes 15 min at a N_2 flow of 1 L min^{-1} for 1 L of sample. Alternatively, the purging flow required to get complete recovery is ≥ 0.75 L min^{-1} with a constant purging time of 20 min. In summary, full recoveries can be achieved if the ratio of purging gas volume to sample volume >15. This agrees well with theoretical estimates based on DEM volatility (*15*).

Evaluation of Analytical Performance. The analytical performance of the DEMA under the optimum working conditions was evaluated in terms of blank, reproducibility, recoveries, and detection limit. Low blank values were obtained from the reference blank (prepurged water) performed in laboratory (90 ± 10 fmol, $N = 10$) or from the procedural purging blank (second analysis) of real samples (average: 100 fmol, range: 60−170; 4 field campaigns, $N = 30$). Excellent reproducibility (rsd ≤ 5%) was achieved during the analyses of spiked estuarine solutions (~0.23 pM; salinity ~20 ppt, $N = 5$) and real samples (salinity 0−30 ppt; DOC 100−700 μM; $N = 5$).

High recoveries of DEM obtained from spiked estuarine water were demonstrated in the discussion section on trap efficiencies. Additionally, we note that on-site DEM determinations of lake waters (DOC range: 300−700 μM C) in Arctic Alaska were conducted during July 2001. The recovery efficiencies, as measured by Hg^0 spiked into the GLS N_2 flow line (~1 L min^{-1}), for the sample trap were 100 ± 10% on average during approximately 300 measurements. It appears that the common degradation of Au-sand trap efficiency caused by water vapor and volatile organic compounds (*16*, *17*) can be prevented by purging with an in-line Teflon syringe filter and precleaning trap and by heating the Au-sand traps at ~600 °C. The high recoveries of spiked waters and real samples demonstrate that this method is accurate and precise.

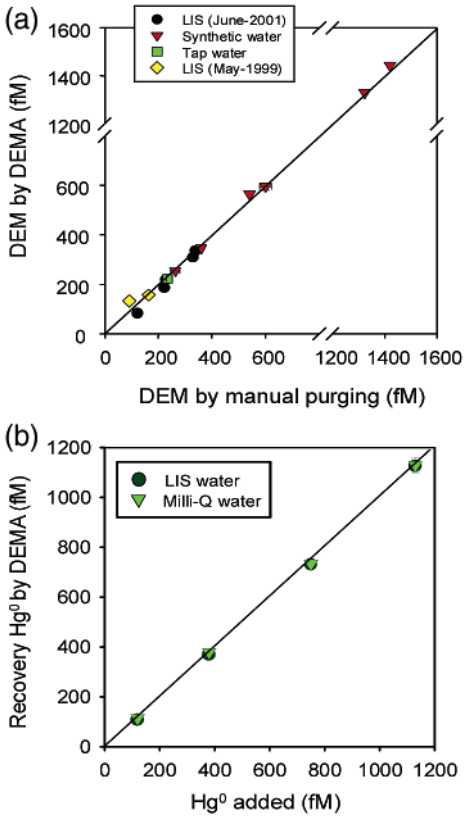

FIGURE 4. Comparison of DEM measured by DEMA with (a) those by manual purging and (b) those with known levels of Hg^0 added. A gaseous Hg standard was injected into a 2.2-L Teflon bottle full of sample water, which was prepurged for 0.5 h at 1 L min^{-1} with purified Hg-free N_2. All the data were collected with the following operating conditions: 1-L sample water, 15 min purging and 1 L min^{-1} of N_2 flow, except for LIS June 2001 using a 2.2-L sample water with 30 min purging (1:1 line plotted for reference).

Calibration ranged from 0.1 to 2.5 pmol in a series of five duplicate gas standard injections, producing a linear relationship ($r^2 = 0.992-0.999$). Good precision (~5%, $N = 22$) in the slopes of calibration curves, conducted by gas injections in 1 L min^{-1} of N_2 purging flow, was obtained during July 2001 for a consecutive 3-week period of operation. The method detection limit, defined as three times the standard deviation of the procedural blank, was about 50 fmol (22 analysis sessions). Sample throughput is ca. 3 samples per hour.

Validation of Method. The proposed method was validated by analysis of several kinds of water samples (i.e. Milli-Q, tap, and LIS waters) with different levels of DEM. As shown in Figure 4a, there was excellent agreement between the manual and the DEMA determinations. Note that traditional manual measurement was conducted with attention to the precautions described in the Introduction. The excellent recovery and agreement of the DEM concentrations, as shown in Figure 4b, indicate again that the DEMA is a robust device for reliable examination and monitoring of DEM in natural waters.

Environmental: DEM Distributions in LIS. We have used the DEMA during several sampling campaigns as part of an EPA STAR program to examine Hg cycling in LIS. DEM data from May and August−September 1999 surveys are presented here. Surface water samples from the axis of Long Island

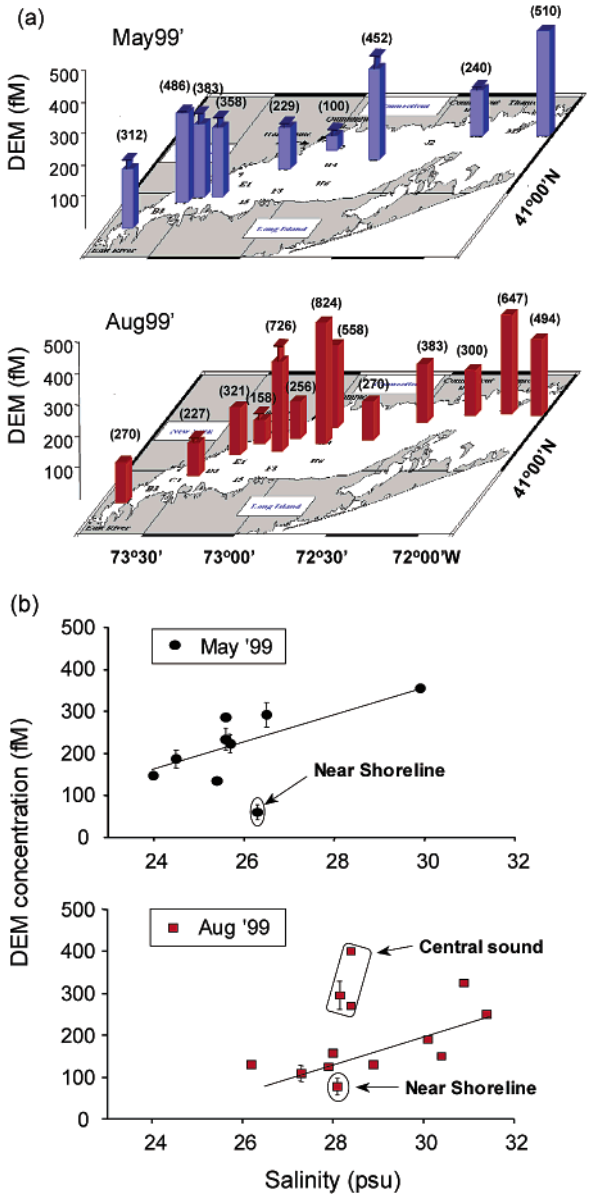

FIGURE 5. Summary of (a) surface DEM concentrations and percent Hg saturation (%S, marked in parentheses) relative to atmospheric equilibrium and (b) surface DEM versus salinity during sampling periods in spring and summer 1999. Errors are ±1 SD ($N = 3$).

Sound (LIS) were collected at some of stations routinely occupied by the Connecticut Department of Environmental Protection for their LIS Water Quality Monitoring Program. Surficial DEM concentration distributions and percent Hg^0 saturation (%S) relative to atmospheric equilibrium are shown in Figure 5a. The overall average DEM concentration was 210 ± 90 fM (mean ± standard deviation, $N = 23$) with a range of 60−400 fM. These results are similar to those (200 ± 130 fM, $N = 42$) reported by Rolfhus and Fitzgerald (*1*) for their four collections in Feb, May, Aug, and Oct during 1995−1997. Our surface samples were supersaturated with Hg^0 (100−820%; atmospheric Hg taken as 15 pmol m^{-3} based on the measurements of Rolfhus (*9*)) relative to atmospheric equilibrium, which indicates that in-situ Hg^0 production is occurring in LIS. The spatial and temporal distributions of DEM varied significantly across LIS. Distribution patterns show DEM maxima in central (associated with elevated concentrations, ca. 300−400 fM, during the summer and lower river flow) and eastern LIS (higher labile Hg near the outflows of Connecticut River and Thames River). This is consistent with the previous LIS DEM surveys in May 1997 and Aug 1995 (*1*). Interestingly, the mid-Sound Hg^0 maxima may be shifted within LIS due to seasonal river flow, which provides the labile Hg species (i.e., reactant/substrate) for Hg^0 production. In the high flow spring season (May 1999), higher DEM concentrations (ca. 270−290 fM) were, for instance, observed westward in western central LIS. Lower DEM was found in western LIS (ca. 130−190 fM) and near the shoreline (ca. 60−80 fM, approaching the detection limit). Furthermore, DEM concentration patterns plotted versus salinity (Figure 5b) show decreases with decreasing salinity toward western LIS (some summer data are higher and do not follow the salinity relationship). This trend is similar to that observed previously by Rolfhus and Fitzgerald (*1*), especially during spring "high flow" conditions. These data suggest that the distribution of DEM is related to the supply and distribution of dissolved labile Hg species (i.e., reactant) controlled by aqueous organic matter (i.e., distribution and nature) present in LIS water. Thus, the production of Hg^0 will be influenced by biological/abiotic reduction processes and delivery of reactant through mixing of surface water.

Hg^0 Flux from LIS. Supersaturation of Hg^0 during our sampling cruises indicates that Hg is lost from the Sound to the atmosphere via evasion. The evasional flux, F, from the surface waters of LIS may be estimated using the oceanic gas exchange equation of Wanninkhof (*18*). This model uses a transfer velocity as proportionality constant by which the air−water concentration gradient is multiplied to estimate the flux. The equation is given by

$$F\ (\text{pmol m}^{-2}\ \text{d}^{-1}) = K(C_W - C_A/H)$$

where K[i.e. transfer velocity (m d^{-1})] = 0.31 u^2 $(Sc^T_{Hg}/660)^{-1/2}$, according to ref *18*, modified for Hg. u^2 is the squared mean wind velocity (m^2 s^{-2}), and Sc is the dimensionless Schmidt number for Hg^0 at temperature T. The constant value of 0.31 is empirically derived. C_W and C_A are respectively the Hg^0 concentrations measured in the surface water and in the overlying air. H represents the dimensionless Henry's law constant of Hg^0, adjusted for sample temperature and salinity (*19*).

Using the data of surface water temperatures (i.e. averaged: 10.6 and 21.7 °C in May and Aug−Sept 1999, respectively), salinities (25.9 and 28.7 psu), and wind speeds (monthly averaged: 4.3 and 3.5 m s^{-1}) collected during the surveys, transfer velocities were estimated at about 1.4 and 1.2 m d^{-1}. Furthermore, using an average of atmospheric Hg value of 15 pmol m^{-3}, salinity-adjusted Henry's law solubility at 10.6 and 21.7 °C of 315 and 444 atm/mole fraction and the observed values of surface water DEM (averaged: 210 and 205 pM), the averaged evasive fluxes from LIS to the atmosphere in May 1999 and Aug−Sept 1999 are calculated to be about 210 and 200 pmol m^{-2} d^{-1}, respectively. The overall averaged flux seems to be comparable with that (ca. 330 pmol m^{-2} d^{-1}) reported in the earlier 1995−1997 work (*1*). The slight difference is, however, as a result of the calculation of u^2 for transfer velocity. Rolfhus and Fitzgerald (*1*) used u^2 as "mean squared u" instead of "squared mean u" used in this paper.

Our studies of DEM in LIS reveal the prominent role of Hg^0 production and evasion in controlling Hg in coast marine environments. High-frequency sampling and analysis is essential for future investigations into the dynamic physical and chemical behavior of Hg^0 in important nearshore regions. Future development of the DEMA can include computer-assisted automation to fulfill the field need of increasing spatial and temporal resolution of DEM patterns in natural waters.

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